NATIONAL BUREAU OF STANDARDS REPORT

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PROGRESS REPORT

August 1, 1966 through March 31, 1967

Development of Methods of Test
For Quality Control of Porcelain Enamels

by

M. D. Burdick and M. A. Rushmer

Porcelain Enamel Institute Research Associateship
National Bureau of Standards
Washington, D. C.

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U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

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SUMMARY

Work is reported on the development of a cleanability test procedure that is based on a water-soluble soil. Several determinations of the cleanability of porcelain enameled surfaces have been made with one water-soluble soil.

Initial steps have been made toward the development of a scratch abrasion test that will, hopefully, correlate with the abrasion damage of porcelain enamels and other surfaces in service.

I. CLEANABILITY

INTRODUCTION

Work previously reported in this series led to a tentative method for determining the cleanability of porcelain enamels. Essentially the method consisted of applying an exact amount of a formulated soiling agent to a specimen surface and then cleaning the surface by a reproducible machine-wiping technique. The residual soil remaining on the specimen, after wiping, was extracted with toluene and the amount of soil was determined by a sensitive fluorescent tracer method. The length of time required to reduce the amount of retained soil to an end-point level was taken as a measure of the cleanability for that surface. The end-point level for all specimens, regardless of color, was based on the visible threshold amount of black soil on a glossy white surface. The work during the present period was aimed at extending the above method of test to a wider range of surfaces through the use of a different soiling agent which could be extracted with a solvent such as water rather than with toluene.

RESULTS AND DISCUSSION

A. The Development of a Water-Soluble Soiling Agent.

A series of soil compositions was prepared in an attempt to find a stable soil with suitable consistency, adherence and covering power. The soil compositions are given in Table 1, together with that of the soil employed in the previous method. The preparations with ethylene glycol as the fluid vehicle became sticky early in the machine-wiping process and showed little promise of being removed in a uniform way with time. Dilution of the ethylene glycol with glycerol made some improvement in the consistency, but the soiled specimen surface became dry during the wiping and no further removal of soil was achieved. Experiments showed that the weight loss by evaporation of soiled specimens continued to increase with time in direct proportion to the ethylene glycol content. This was thought to represent an unstable condition which could not be avoided with this vehicle. The soils with a glycerol base, on the other hand, were shown to exhibit no weight change during use. The fluorometer was calibrated with soils VII and VIII for further quantitative experiments.

B. Modifications of the Previous Techniques.

1. A muslin covered soiling head, previously used, was replaced by a one-inch diameter brass head, the bottom surface of which was faced with a one-sixteenth-inch thick covering of teflon. The new head uniformly distributed the soil and avoided its absorption (on the muslin) during the one minute soiling treatment.

2. The amount of soiling agent required for a test was reduced.

3. Paper tissues were used during the first minute of the cleaning treatment; the first for ten seconds, the second for twenty seconds and the third for thirty seconds. Additional cleaning was achieved by a muslin covered

head which material proved to be more durable than cleaning tissue during the longer cleaning periods, particularly on non-glossy finishes. It was thought that the "sizing" normally applied to unbleached muslin might interfere with soil absorption, and that more uniform results might be obtained with laundered and "ironed" material. An analysis of variance applied to experimental results indicated that a greater soil removal was achieved when laundered muslin was used but no gain in repeatability was achieved. For this reason the additional steps of laundering and ironing were discarded.

4. A brass extraction device was developed. The previous method required a definition of the area from which soil was to be extracted by hand-cleaning the soiled specimen except under a mask of known area. This was time consuming and perhaps subjective. The remaining soil from the masked area was then removed by the toluene solvent contained in a bottomless glass bottle clamped against a teflon gasket and the specimen. Problems of gasket leaks, particularly with matte finishes, were encountered. No other more flexible or compressible gasket material was found which was inert to toluene.

The adoption of a water solvent, in the current modification of the test, allowed the use of a pliable, rubber O-ring for the dual purpose of defining the area of extraction and forming a leak proof seal against specimen surfaces. A bottomless brass bottle was prepared which could be sealed at the top with a rubber stopper. An O-ring was inserted into a groove in the bottom edge of the brass container. When this device was clamped against a soiled specimen a leak proof seal was achieved because of the compressibility of the rubber and, at the same time, the area of the specimen from which soil was to be extracted was defined in a reproducible manner. The spot-masking operation previously used, was completely avoided.

C. Cleaning Rate Curves of Porcelain Enamels, Using Glycerol-Based Soiling Agents.

Previous work has indicated the marked linearity of log-log plots of soil retained and cleaning time, after periods of cleaning between one and sixty minutes, when an oily soiling agent was employed. Data were needed to show whether glycerol-based soils could be mechanically removed in such a way that the logarithm of the soil remaining was proportional to the logarithm of cleaning time. The data plotted in Figure 1 were obtained on two porcelain enamels using two somewhat similar glycerol-based soiling agents. Each data point in Figure 1 represents the average of six individual specimens similarly soiled and cleaned. The horizontal displacement of the two curves may be attributed not only to differences in enamel characteristics and textures but also to differences in response to cleaning of the two soiling agents used. In Table 2, where data were obtained on these same two porcelain enamels, both employing Soil VIII, the cleaning time required to reduce the residual soil to the end-point level of one microgram per square centimeter was 6.1 and 3.3 minutes for enamels D and R respectively.

D. The Selection of an End-Point for the Test.

The cleaning rate curves, discussed above, may be used to estimate the time required to reduce the soil on a specimen surface to any desired level of cleanliness. It was desired to select a suitable level of cleanliness for use as an end-point in the test.

A series of similar specimens of a glossy, white porcelain enamel (R, Figure 1) were soiled with Soil VIII and cleaned for various times between 0.5 and 4 minutes. The amounts of soil remaining after these treatments were shown in Figure 2. Spots at the specimen center were masked and cleaned around so that each specimen was clean except for a 1 1/4-inch diameter undisturbed spot at its center. Two "blank" specimens (unsoiled) were added to the series. Several observers were asked to indicate which spots they could see. The results are shown in Figure 2. Observers with the sharpest visual acuity and/or best lighting were able to distinguish spots with 0.9 and 1.1 $\mu g/cm^2$ from the blanks. On this basis 1.0 $\mu g/cm^2$ was selected as a practical end-point for the test, which had for its basis the threshold value below which Soil VIII was not visible on a white specimen surface. This level was shown as a horizontal dashed line at 1.0 $\mu g/cm^2$ in Figure 1.

E. The Calculation of a Cleanability Index.

It is suggested that a cleaning rate curve be determined by extracting residual soil from six specimens cleaned for one or two minutes and from six specimens cleaned for six or more minutes. The intersection of the curve through the above determined points with the end-point level of 1.0 $\mu g/cm^2$ in units of cleaning time may be used as a cleanability index for that surface.

F. Results on a Group of Glossy Porcelain Enamels.

Preliminary determinations on nine porcelain enamels are given in Table 2. Certain of these enamels (A, B, D, E & F) were previously reported using the oily soil GF. Table 2 shows these five surfaces to have cleanability indices of between 4 and 7 minutes with the water soluble soil here described. Indices

of between 2 and 5 minutes were obtained with the oily soil previously used. This may be interpreted to indicate that these surfaces (all glossy) have somewhat similar cleanability indices by which ever method used.

PLANS FOR THE NEXT REPORT PERIOD

1. Determine the repeatability of cleanability indices for a given surface.

2. Seek a correlation between this method for measuring cleanability and some other estimate of this property.

3. Determine the applicability of this technique and these reagents, or modifications thereof, to a selection of surfaces other than procelain enamels.

II SCRATCH-ABRASION

INTRODUCTION

The Porcelain Enamel Institute has had a standard abrasion test since 1939 [1/]. This test abrades the uneven porcelain enameled surfaces uniformly and is extremely reproducible. It is thought that this test gives a measure of the inherent abrasion resistance of a porcelain enamel. However, variables in processing may produce enamels that do not show their inherent abrasion resistance in service. This non-correlation of service and PEI abrasion was noted by Crandall in 1952 [2/].

When M. D. Burdick first started his study of cleanability of porcelain enamels he noted that the abrasion in the PEI abrader did not resemble that which occurred by abrading a specimen with a commercial cleanser and a hand brush. The PEI abrader opened a series of sub-surface pores while the hand abrasion produced random scratches and opened only a very few sub-surface pores (For illustrations see NBS Report #8624, Oct.-Dec. 1964, in this series). He also found that the results obtained by hand abrading could be duplicated qualitatively, by using the lapping device used in the cleanability procedure and abrading for five minutes with a slurry of 600 grit silicon carbide and water. The purpose of the current work is to modify the abrasion method outlined by Burdick to a quantitative method of measuring the degree of surface or scratch-abrasion.

RESULTS AND DISCUSSION

A. Measurement of the Degree of Abrasion Damage.

Before any test for abrasion resistance can be promulgated, it is essential that there be some "yardstick" or method available to measure the degree of damage caused by the abrasion. In the past the degree of abrasion has been measured by either 1) loss in gloss or 2) loss of weight. Since the scratch-abrasion under consideration causes only minor damage to the surface, the measurement of weight loss would be almost impossible and the differences in gloss from one orientation to another on the same specimen were often larger than differences obtained by abrasion. This indicated that a new or different "yardstick" was needed. Two such measures are now being considered.

1. Change in Haze

Haze is an optical measurement of the roughness of the specimens surface. It is the ratio of the light scattered by a clear plastic replica of the surface to the light transmitted by the replica. By making replicas both before and after abrading, the degree of abrasion damage may be taken as the difference in the haze of the two replicas. The actual haze measurements are quick and easy, however, extreme care must be exercised in making the replicas to duplicate the surface in question.

2. Change in Soil Retention

One of the major effects of abrasion of a porcelain enameled surface in service is the increase in soil retention of the surface. It, therefore, seemed logical to use the change in soil retention before and after abrasion as a method of measuring the abrasion damage. Two methods for determining the soil retention have been used. These will be referred to as methods C and D later in this report. Method C consisted of using an oil base soil (GF in Table 1) and cleaning for six minutes while method D consisted of using

a water-soluble soil, (VIII in Table 1) and cleaning for two minutes. In both methods C and D the soil remaining after cleaning is determined by fluorometric analysis. (For further details on the procedure see the Cleanability section of this and preceding reports).

B. Abrasion

The general procedure followed has been to tape a specimen to a lap which rotates at 156 rpm. A one inch diameter plastic covered brass head then spreads an abrasive slurry back and forth over the specimen surface at approximately six cycles per minute. The variables of lubricant, abrasive, and time all have some effect on the end results. Some attempt has been made to select these variables to give the maximum scratch-abrasion in the minimum time.

1. Effect of Lubricant

The first trials were made using water as a lubricant. This proved quite unsatisfactory since it partially evaporated and formed a very thick slurry which often caused the abrading head to tip instead of changing direction. For this reason the lubricant was changed to paraffin oil and this difficulty was eliminated. A trial was also made to compare the effect of abrading dry versus abrading the specimen with a slurry of silicon carbide and paraffin oil. The results are shown below:

Enamel	Change in Soil Retained		Abrasive	Abrasion
	Dry	Mineral Oil		Time
5	0.4	4.3	400 SiC	4 1/2 min.

Thus the use of oil appears to leave the abrasive particles free to rotate and bear new cutting edges whereas the abrasive particles tend to pack together under the abrading head when it is used dry.

2. Abrasive

So far three grades of abrasive have been used: 600, 400 and 100 silicon carbide. Either the 400 or the 600 produce random scratch patterns of well defined scratches, but the 400 will reduce the haze in five minutes the same amount as the 600 will in ten minutes. The 100 silicon carbide produced an even greater reduction in haze per abrading time, however, spalling occurred around the scratches and this is thought to be undesirable. Considering both the time and the type of scratch produced, 400 mesh silicon carbide has been selected for the work to date.

3. The Effect of Abrasion Time.

The data for change in both haze and soil retention for two glossy enamels abraded for different times are presented in Table 3 and Figure 3. Figure 3 illustrates two rates of change in soil retention as a result of scratch-abrasion. The initial rate is thought to be caused by scratching through the fire polished surface while the second rate is thought to occur as the tops of the orange peeled surfaces are slowly worn down revealing the subsurface bubble structure. If the abrasion were continued, the change in soil retention should eventually reach a constant value when all the fire polished surface is removed.

C. Differentiation of the Scratch-Abrasion Resistance of Enamels.

Ten different enamels were abraded by placing 0.15 ml of paraffin oil on the specimen and spreading it around for 30 seconds, adding 0.025 g of 400 silicon carbide to the specimen and abrading for 4 1/2 minutes. After abrading, the specimens were washed with liquid detergent on a soft sponge to remove the excess mineral oil and abrasive. These specimens were measured for dirt retention both before and after abrasion by method C and replicas of the specimen's

surfaces were measured for changes in haze. These results are given in Table 4. The data in this table indicate that either the change in soil retention or haze will indicate a difference in scratch-abrasion resistance. However, they did not indicate the same differences.

D. Instrumental Estimation of Abrasion vs Visual Estimates.

When developing a test to correlate with use, it is important to keep instrumental estimates of abrasion in line with visual estimates. Therefore, eight of the specimens (white enamels only) listed in table 4 were given to four observers who were asked to rank them according to the amount of abrasion damage. These visual rankings did not agree with either method of instrumental ranking. It was noted that the differences in specimen texture (from mat to glossy) made visual evaluations of damage difficult. Therefore, two glossy enamels were abraded for various lengths of time and again given to the four observers for ranking according to abrasion damage. The average rank for the observers is plotted verses the instrumental rank in figure 4. Here it can be seen that a nearly perfect correlation exists between the ranking by instrumental and visual estimates of damage when differences in specimen texture are not present.

PLANS FOR NEXT REPORT PERIOD

During the next report period it is planned to 1) determine the reproducibility of this test method, 2) see how the results obtained with the PEI abrader correlate with the scratch-abrasion, 3) to determine whether this method of abrasion could be used on competitive finishes, and 4) to see if the PEI abrader could be modified to produce the same type of abrasion as produced with the current lapping method.

III. CONTINUITY OF COATING

A round-robin test to determine the calibration curves for different AC high-voltage test equipment is under way. These results will be reported when all laboratories have completed the Calibration.

IV. WEATHERING TESTS

A report of the results of the one-year inspection of the 1964 Exposure Test of Porcelain Enamels on Aluminum was prepared for the sponsors and the exposure specimens were returned to the racks at all exposure sites. The next inspection of these specimens is planned after three-years exposure.

The enamels in the 1966 Exposure Test for Nature-Tone enamels on Steel have been exposed at Kure Beach, North Carolina - 80 feet from the ocean, and Miami, Florida. These specimens will be returned for their six-month inspection during the next report period. It is also hoped that the specimens will be installed at Gaithersburg, Maryland during the next report period.

REFERENCES

1. "Test for Resistance of Porcelain Enamels to Abrasion", Bulletin T-2, Porcelain Enamel Institute, 1900 L St., N. W., Washington, D. C. 20036. See also ASTM C448 "Abrasion Resistance of Porcelain Enamels."

2. J. R. Crandall, "Correlation of Laboratory and Service Data on Poreclain Enamels", Proceedings of the PEI Forum, p. 160, 1952.

TABLE 1. WATER SOLUBLE SOILING AGENTS

Ingredients	I	II	III	IV	V	VI	VII	VIII	GF [a/]
Ethylene Glycol	70.0	88.9	47.0	62.4	--	--	--	--	--
Glycerol	--	--	29.3	10.9	73.3	73.0	49.8	72.9	--
S-Lube (7.5% solids) [b/]	20.0	5.5	20.8	24.7	24.7	--	24.9	26.0	--
GP-180 (30.0% solids) [b/]	--	--	--	--	--	25.0	--	--	--
Uranine [c/]	10.0	5.6	2.9	2.0	2.0	2.0	2.0	1.0	--
Distilled Water	--	--	--	--	--	--	23.3	--	--
Detergent	--	--	--	--	--	--	--	0.1	--
Paraffin Oil	--	--	--	--	--	--	--	--	42.3
Oildag	--	--	--	--	--	--	--	--	57.4
BBOT [d/]	--	--	--	--	--	--	--	--	0.3

a/ Oily soil used in previous reports

b/ S-Lube and GP-180 are commercially available dispersions of colloidal graphite in water and were obtained from Graphite Products Corporation, Brookfield, Ohio.

c/ Uranine is the sodium salt of Fluorescein, $C_{20}H_{10}O_5Na_2$. In water this compound forms a yellow solution which has a very intense greenish fluorescence which may be observed under ordinary conditions in 40 million parts diluent. With refined method of fluoro-analysis it may be detected 1:200 million or even greater.

d/ BBOT represents 2, 5-bis [2-(5-tert-Butylbenzoxazolyl)] - thiophene

TABLE 2 CLEANABILITY INDICES FOR SOME PORCELAIN ENAMELS USING WATER-SOLUBLE SOIL VIII

Designation	Soil Retained [a/]		Cleanability Index
	2 min. cleaning time µg/cm²	6 min. cleaning time µg/cm²	minutes
Q	1.20	0.70	2.9
R	1.52	0.62	3.3
A	1.40	0.77	3.7
F	1.42	0.81	3.9
B	2.05	0.76	4.4
D	2.25	1.02	6.1
E	1.81	1.09	7.3
S	2.23	1.14	7.3
T	2.13	1.20	8.5

[a/] Each value for soil retained is the average for six specimens.

TABLE 3 Effect of Abrasion Time on the Change of Both Haze and Soil Retention

Abrasion Time	Enamel 5		Enamel 2	
	Change in Soil Retained	Change in Haze	Change in Soil Retained	Change in Haze
(minutes)	($\mu g/cm^2$)	(%)	($\mu g/cm^2$)	(%)
1	0.4	-0.2	2.0	4.0
2	1.9	0.8	3.1	4.5
4	2.8	2.8	6.7	8.5
8	7.1	4.8	7.5	12.5
16	9.3	6.8	9.6	17.0

TABLE 4 Comparison of Enamels Abraded 4 1/2 Minutes with 400 Silicon Carbide and Paraffin Oil

Enamel	Soil Retained - ($\mu g/cm^2$)			Haze (%)		
	New	Abraded	Change	New	Abraded	Change
E-115	0.1	1.1	1.0	52.3	54.8	2.5
NT	0.6	1.9	1.3	53.0	50.8	-2.2
BA	0.5	2.1	1.6	10.6	12.6	2.0
ZB	0.8	3.2	2.4	3.0	8.6	5.6
C	0.4	4.3	3.9	3.0	5.7	2.7
5	0.8	5.1	4.3	2.7	6.0	3.3
V	0.2	7.4	7.2	4.0	6.5	2.5
2	0.7	8.5	7.8	3.0	11.3	8.3
4	1.3	12.8	11.5	3.7	6.2	2.5
R	0.9	46.1	45.2	4.0	9.8	5.8
P	1.9	60.6	58.7	3.8	11.1	7.3

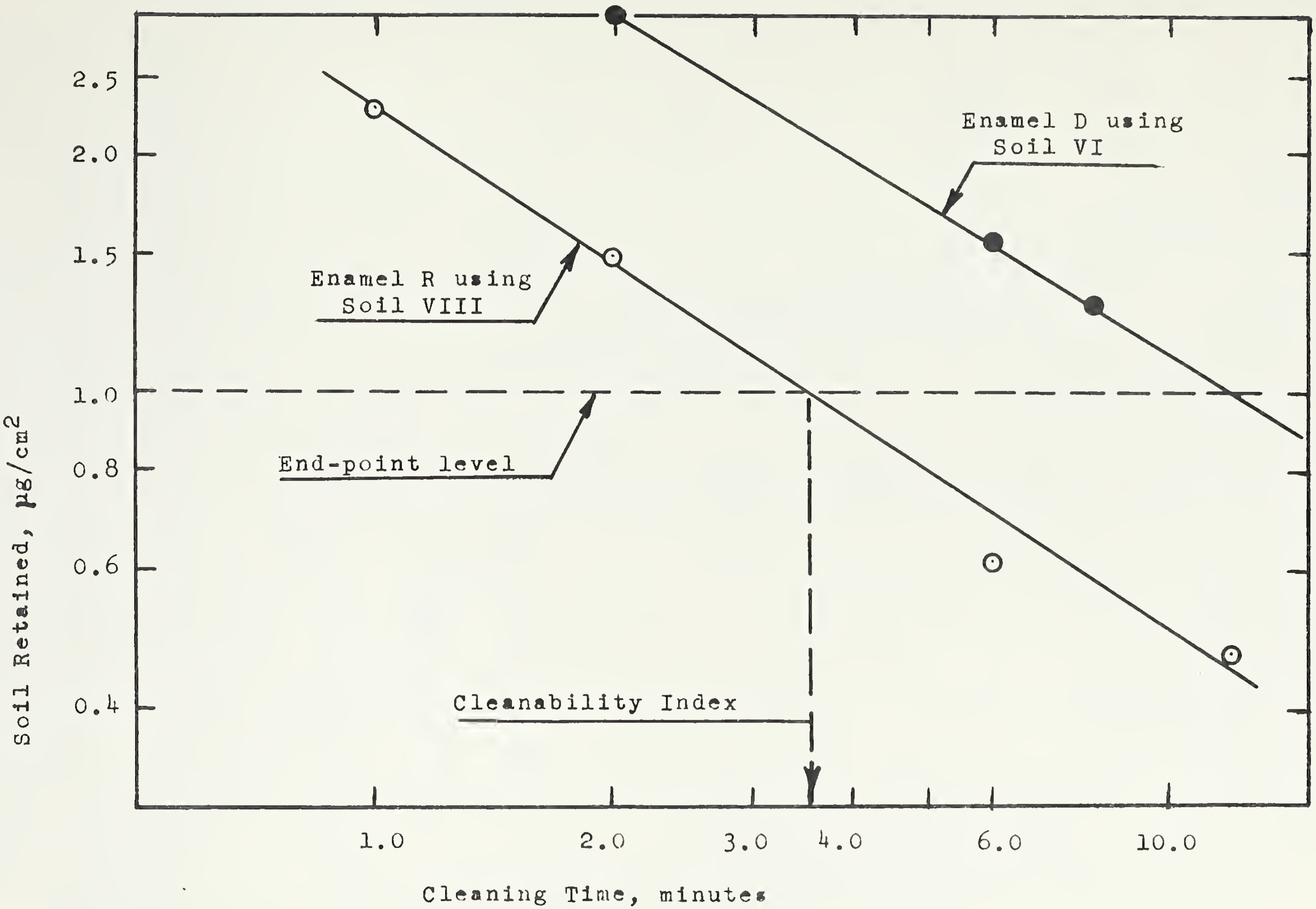
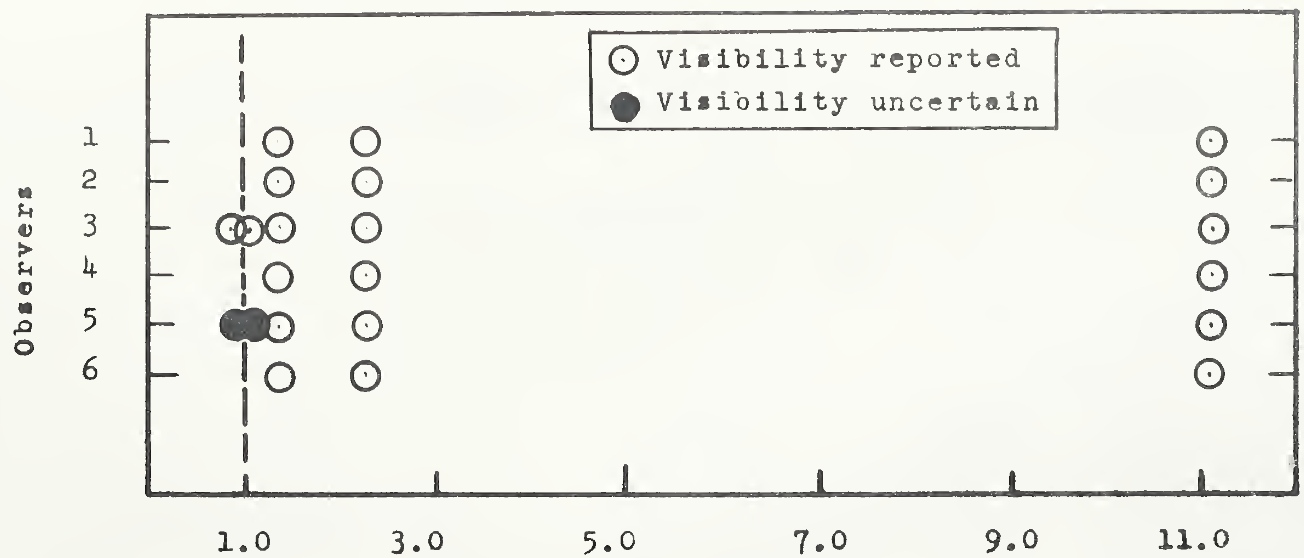


Figure 1. Cleaning Rate Curves for Two Porcelain Enamels.



Specimens Used in the Experiment

Cleaning time minutes	Soil Retained $\mu g/cm^2$
0.5	11.1
1.0	2.3
2.0	1.4
3.0	1.1
4.0	0.9
---	Blank
---	Blank

Figure 2. The Visible Threshold of Soil VIII on White Porcelain Enamel

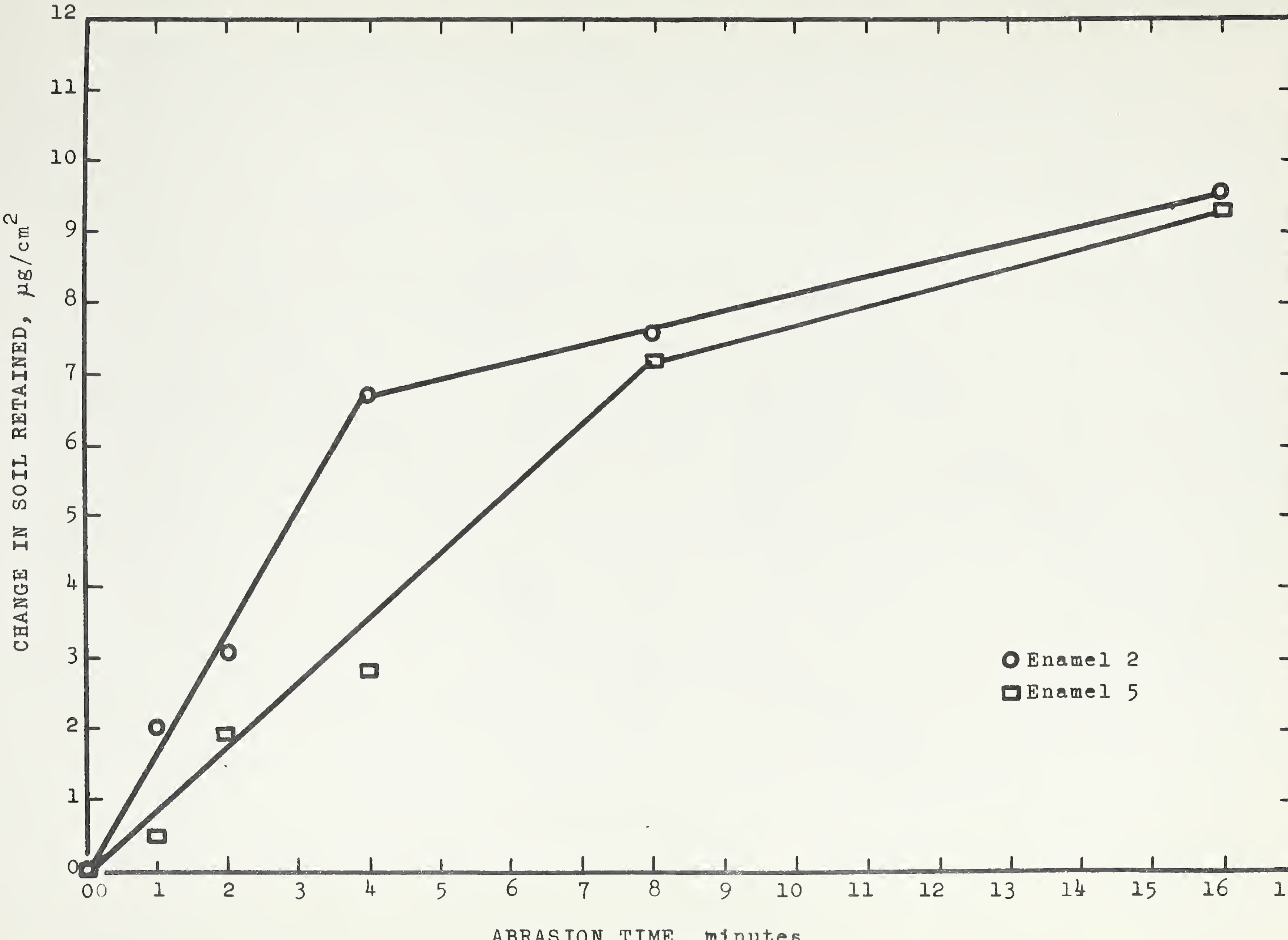


Figure 3. Effect of Abrasion Time on the Change in Soil Retained

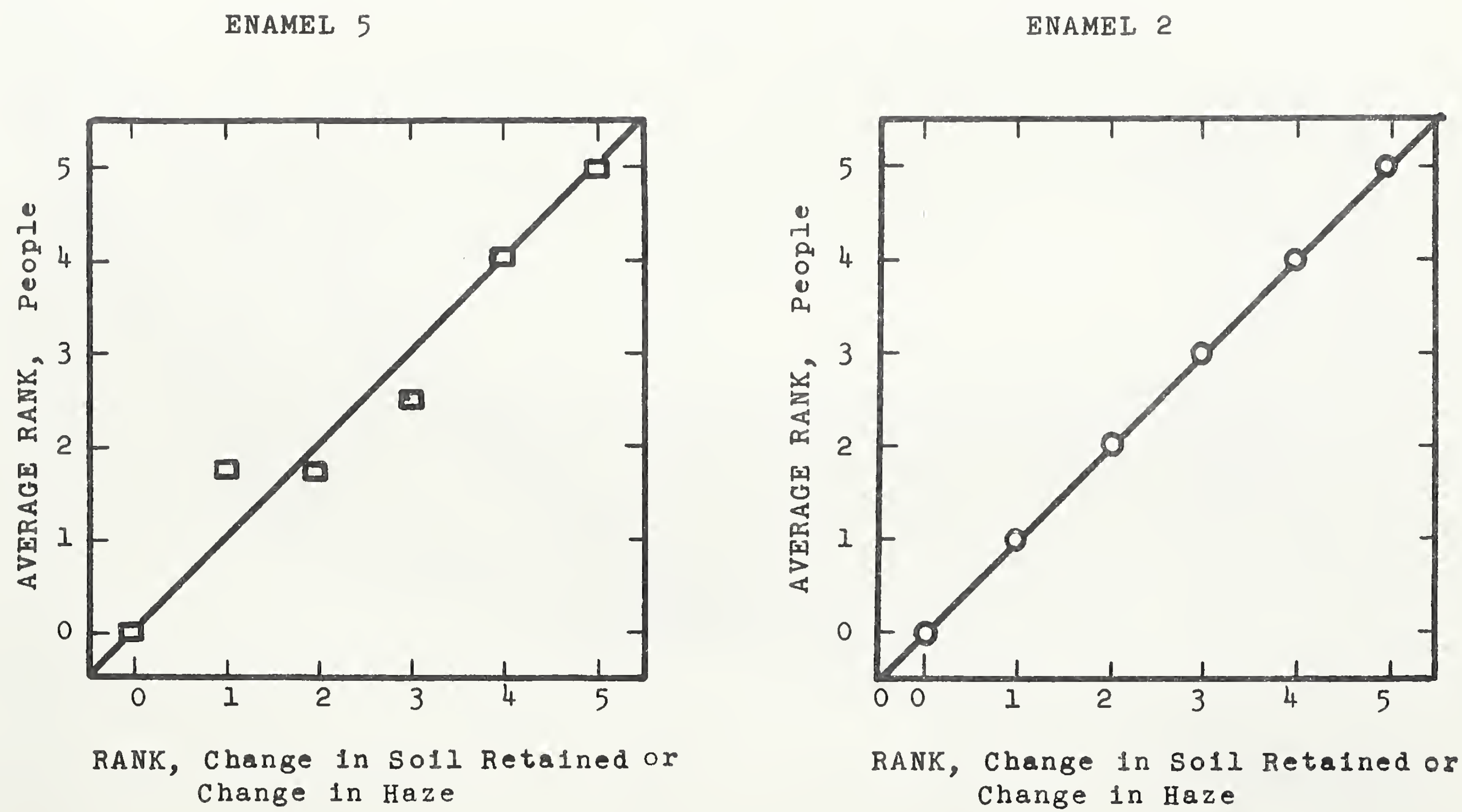


Figure 4. Comparison of the Amount of Abrasion Damage as Estimated by Visual Observation and by the Change in Soil Retained or the Change in Haze.

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